# Matching a Diffusive and a Kinetic Approach for Escape over a Fluctuating Barrier

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(Received 9 June 1993)

We study thermally driven escape over a dichotomously fluctuating barrier and present explicit formulas for the mean escape time in three limiting frequency domains. Our analysis is based on the chemically realistic case of large potential barrier, and modest fluctuation amplitude. When the fluctuation frequency is small compared to the time scale for adiabatic adjustment, which includes the low and intermediate frequency regimes, a kinetic approximation reproduces the Fokker-Planck results.

PACS numbers: 82.20.Mj, 02.50.−r, 05.40.+j

Recently Doering and Gadoua [1] reported results concerning the escape rate over a fluctuating barrier such as depicted in Fig. 1. They started from a Langevin equation and transformed it into a Fokker-Planck equation (FPE), from which they derived an expression for the mean first passage time (MFPT) as a function of system parameters. A graph such as the solid line in Fig. 2 was found for ln(MFPT) as a function of $\ln\gamma$, where $\gamma$ represents the flipping rate of the Markovian fluctuation of the barrier between $E_0+\Delta E$ and $E_0-\Delta E$. The left, low frequency limit could be identified with the average of the passage times over the high $(E_0+\Delta E)$ and low $(E_0-\Delta E)$ barrier. The right, high frequency limit could be identified with the MFPT over the average $(E_0)$ barrier. The minimum that occurs in between was characterized by Doering and Gadoua as "resonant activation." This result has generated some astonishment [2]. The above authors [1] only obtained a manageable closed form expression for the single exceptional case where $E_0=0$. This means that the potential was actually flipping between a barrier and a well. They also showed results for another case where the barrier flipped between $8kT$ and 0, and conjuctured that the results might be applicable to a wider range of situations. Below we study the physicochemically important case [3] where $\Delta E/E_0$ is small and we indeed find a similarly shaped curve (see Fig. 2). An asymptotic analysis of the Fokker-Planck equation allows us to obtain three simple limiting expressions for the MFPT in three well defined frequency regimes. With this analysis the presence of the minimum is all but mysterious and its location can be derived with astonishingly simple mathematics. Additionally, we show that a formulation in terms of a chemical kinetic model accurately describes the behavior in the low and middle frequency regions.

The original Langevin equation is

$$\beta\dot{x} = -\frac{d}{dx}V(x,t)+\sqrt{2\beta kT}\xi(x,t)\,, \tag{1}$$

where $\beta$ represents the coefficient of viscous friction and $\xi(t)$ stands for normalized white noise. The potential $V(x,t)$ is piecewise linear and dichotomously fluctuating

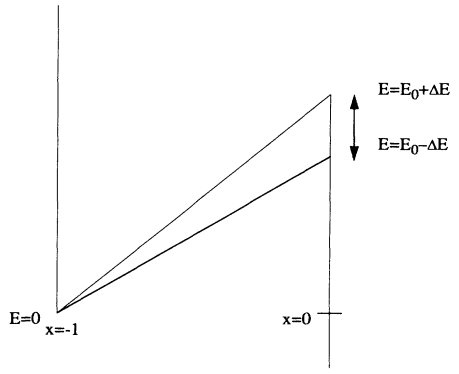



FIG. 1. Setup for the problem. The height of the barrier fluctuates between $E_0+\Delta E$ and $E_0-\Delta E$.

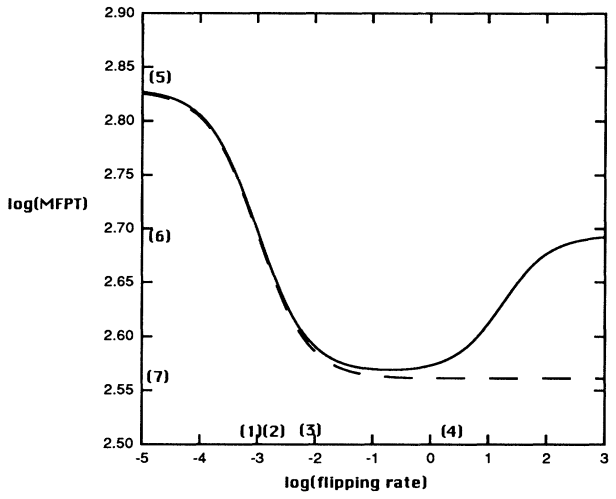



FIG. 2. The log of the mean first passage time versus the log of the barrier fluctuation rate for the case with $E_0=11$ and $\Delta E=1$. The solid line is a numerical computation of Eq. (8) using Eq. (6) to calculate the eigenvalues $\lambda_i$ and using Eq. (9) to calculate the $A_i$. The dashed line is the result of computing Eq. (11), which, as we discussed, is identical to the kinetic model Eq. (15) with the rate constants of Eq. (16).

0031-9007/93/71(10)/1649(4)$06.00

(see Fig. 1). After absorbing $\beta$ in the time scale, and taking $kT$ as the unit of energy, the joint probability distribution $\rho_{\pm}(x,t)$ that the particle is at $x$ and that the potential is in the up (+) or down (−) configuration is given by the following FPE:

$$\frac{\partial}{\partial t}\begin{bmatrix}\rho_+\\ \rho_-\end{bmatrix}=\begin{bmatrix}-\gamma+(E_0+\Delta E)\partial_x+\partial_{xx} & \gamma\\ \gamma & -\gamma+(E_0-\Delta E)\partial_x+\partial_{xx}\end{bmatrix}\begin{bmatrix}\rho_+\\ \rho_-\end{bmatrix}, \tag{2}$$

where $\gamma$ denotes the flipping rate of the dichotomously fluctuating barrier. We start with the particle at the bottom ($x=-1$), so the initial condition is

$$\rho_{\pm}(x,0)=\tfrac{1}{2}\delta(x+1). \tag{3}$$

The boundary conditions for the reflecting ($x=-1$) and absorbing ($x=0$) boundary, respectively, are

$$\begin{aligned}&-[(E_0\pm\Delta E)+\partial_x]\rho_{\pm}(x,t)|_{x=-1}=0,\\ &\rho_{\pm}(0,t)=0.\end{aligned} \tag{4}$$

Using standard methods described in Secs. 3.6 and 5.2.7 of Ref. [4] this system is reduced to a system of two coupled ordinary differential equations, from the solution of which the MFPT can be deduced:

$$\begin{aligned}&F''(x)-(E_0+\Delta E)F'(x)-\gamma F(x)+\gamma G(x)+\tfrac{1}{2}=0,\\ &G''(x)-(E_0-\Delta E)G'(x)-\gamma G(x)+\gamma F(x)+\tfrac{1}{2}=0.\end{aligned} \tag{5}$$

Here, $F(0)=G(0)=0$ for the absorbing barrier and $F'(-1)=G'(-1)=0$ for the reflecting barrier. The MFPT $\langle\tau\rangle$ for a particle that starts at the bottom ($x=-1$) is $\langle\tau\rangle=F(-1)+G(-1)$. Taking $S_0=F+G$, $S_1=F'+G'$, $D_0=F-G$, and $D_1=F'-G'$ we derive

$$\begin{bmatrix}S_0'\\ S_1'\\ D_0'\\ D_1'\end{bmatrix}=\begin{bmatrix}0&1&0&0\\ 0&E_0&0&\Delta E\\ 0&0&0&1\\ 0&\Delta E&2\gamma&E_0\end{bmatrix}\begin{bmatrix}S_0\\ S_1\\ D_0\\ D_1\end{bmatrix}+\begin{bmatrix}0\\ -1\\ 0\\ 0\end{bmatrix}, \tag{6}$$

with $S_0(0)=S_1(-1)=D_0(0)=D_1(-1)=0$ and $\langle\tau\rangle=S_0(-1)$. This system decouples; we can solve for $S_1$, $D_0$, and $D_1$ and obtain the MFPT as $S_0(-1)=-\int_{-1}^{0}S_1(x)dx$. The general solution of the $S_1$, $D_0$, and $D_1$ system is

$$\begin{aligned}&S_1(x)=A_1e^{\lambda_1x}+A_2e^{\lambda_2x}+A_3e^{\lambda_3x}+\frac{1}{E_0},\\ &D_0(x)=B_1e^{\lambda_1x}+B_2e^{\lambda_2x}+B_3e^{\lambda_3x}-\frac{\Delta E}{2\gamma E_0},\\ &D_1(x)=C_1e^{\lambda_1x}+C_2e^{\lambda_2x}+C_3e^{\lambda_3x},\end{aligned} \tag{7}$$

where $\lambda_1$, $\lambda_2$, and $\lambda_3$ are the three eigenvalues of the matrix of the homogeneous part of the $S_1$, $D_0$, and $D_1$ system. After solving this system the MFPT can be expressed as

$$\langle\tau\rangle=\frac{A_1}{\lambda_1}(e^{-\lambda_1}-1)+\frac{A_2}{\lambda_2}(e^{-\lambda_2}-1)+\frac{A_3}{\lambda_3}(e^{-\lambda_3}-1)-\frac{1}{E_0}. \tag{8}$$

The boundary conditions along with the equality $D_1=D_0'$ provide relations between the free constants $A_i$, $B_i$, and $C_i$. We obtain a linear algebraic system for $A_1$, $A_2$, and $A_3$:

$$\begin{bmatrix}e^{-\lambda_1} & e^{-\lambda_2} & e^{-\lambda_3}\\ (\lambda_1-E_0)/\lambda_1 & (\lambda_2-E_0)/\lambda_2 & (\lambda_3-E_0)/\lambda_3\\ e^{-\lambda_1}(\lambda_1-E_0) & e^{-\lambda_2}(\lambda_2-E_0) & e^{-\lambda_3}(\lambda_3-E_0)\end{bmatrix}\begin{bmatrix}A_1\\ A_2\\ A_3\end{bmatrix}=\begin{bmatrix}-1/E_0\\ \Delta E/2\gamma E_0\\ 0\end{bmatrix}. \tag{9}$$

The three eigenvalues can be developed as a series in $\gamma$:

$$\begin{aligned}&\lambda_1=\frac{2E_0}{E_0^2-\Delta E^2}\gamma+\frac{4E_0(E_0^2+\Delta E^2)}{(E_0^2-\Delta E^2)^3}\gamma^2\cdots,\\ &\lambda_2=(E_0-\Delta E)+\frac{1}{(E_0-\Delta E)}\gamma\cdots,\\ &\lambda_3=(E_0+\Delta E)+\frac{1}{(E_0+\Delta E)}\gamma\cdots.\end{aligned} \tag{10}$$

For sufficiently small $\gamma$ (with large $E_0$ and moderate $\Delta E$) we can drop all but the first term in each of these series. For $E_0=11$, $\Delta E=1$, and $\gamma=1$ (in which case, as we will see later, the flipping time is much smaller than the MFPT over the low and high barriers and about the same as the MFPT over a zero barrier) the second term in each of the series is more than 50 times as small as the first term. Further expansion just shows that the coefficients of the higher order terms, $\gamma^n$ are decreasing as rapidly as $O(E_0^{1-2n})$. Next, neglecting the $\Delta E$ in $(E_0\pm\Delta E)^2$ except when $(E_0\pm\Delta E)^2$ appears in an exponent, we derive manageable expressions for $A_1$, $A_2$, and $A_3$. We find that under these conditions (small $\gamma$, large $E_0$, and moderate $\Delta E$) we can also neglect all but $-(A_2/\lambda_2+A_3/\lambda_3)$ in the expression for the MFPT. We arrive at

$$\langle\tau\rangle\approx\frac{E_0^2e^{-E_0+\Delta E}+E_0^2e^{-E_0-\Delta E}+4\gamma}{2[E_0^4e^{-2E_0}+(E_0^2e^{-E_0+\Delta E}+E_0^2e^{-E_0-\Delta E})\gamma]}. \tag{11}$$

Figure 2 shows the approximation (11) and a numeri-

cal calculation based on (8) for $E_0=11$ and $\Delta E=1$. The three important points on the $\ln\gamma$ axis are the points where the flipping time equals the MFPT over the high barrier, the MFPT over the low barrier, and the MFPT over the zero barrier. These points are indicated in Fig. 2 and in Table I with the numbers (1), (3), and (4), respectively. For the sets of parameter values that Doering and Gadoua took ($E_0=0,\Delta E=8$ and $E_0=4,\Delta E=4$) the ln(MFPT) of the low barrier was equal or very close to the ln(MFPT) over a zero barrier, but for the parameter values that we took these points are well spread out. The domain where the flipping time is of the order of the MFPTs over the high and low barrier appears to be well within the range of validity of approximation (11). The minimum occurs for the flipping time being much larger than these MFPTs and corresponds to the $\gamma\rightarrow\infty$ limit of (11). Expression (11) is a sigmoidally shaped function of $\gamma$ and for our values of $E_0$ and $\Delta E$ the inflection point of the sigmoid occurs when the average flipping time of the barrier is in between the MFPTs of the low and high barrier (see Fig. 2 and Table I). Interestingly, the MFPT at the inflection point is exactly the same as the high frequency limit. Agreement between approximation (11) and the actual solution starts to break down when the flipping time equals the MFPT over the zero barrier.

A similar expansion in powers of $1/\gamma$ can be made to allow evaluation of the very high frequency limit,

$$\lambda_1=E_0-\tfrac{1}{2}E_0\Delta E^2\gamma^{-1}+\cdots,$$
$$\lambda_2=\sqrt{2\gamma}+\tfrac{1}{2}E_0+\cdots, \qquad (12)$$
$$\lambda_3=-\sqrt{2\gamma}+\tfrac{1}{2}E_0+\cdots.$$

These series lead to an MFPT that for $\gamma\rightarrow\infty$ asymptotically approaches $E_0^{-2}\exp(E_0)$ from below.

By setting $\gamma=0$ and $\Delta E=0$ in Eq. (6) the MFPT over a constant barrier of height $E_0$ is found to be

$$\langle\tau\rangle=(1/E_0^2)(e^{E_0}-1-E_0). \qquad (13)$$

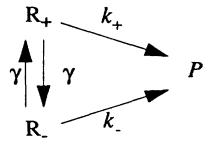
For sufficiently large $E_0$ the linear and the constant terms can be neglected relative to the exponential and we have $\langle\tau\rangle\approx E_0^{-2}e^{E_0}$. For $\Delta E\approx 1$ and $E_0>10$ the low barrier MFPT is about a tenth of the high barrier MFPT and can be neglected. This leads to some very simple formulas for the locations of important time scales of the system, these formulas are given in Table I. The time scales are also indicated in Fig. 2.

Kramers, in his classic 1940 paper [5], showed that under certain circumstances diffusion over a single potential barrier can be modeled in terms of transitions occurring between two states. This leads to a formulation that is mathematically described by a single first order ordinary differential equation in which the escape rate is given in terms of a rate constant multiplied by a concentration. In our case (Fig. 1), this concentration is the probability density integrated from $-1$ to 0. In many cases, the effects of fluctuations of the barrier height can be modeled in terms of an extended kinetic scheme [6-8] which explicitly includes the reactions over both high and low barriers and transitions between the high and low barriers.

TABLE I. Different time scales for our model. The formulas are approximations for the case of sufficiently small $\Delta E/E_0$ and sufficiently large $\exp(2\Delta E)$. Our results for the MFPTs and flipping times are for time units scaled by the viscous friction and a potential well of unit length. To get back to the values with physical dimensions (i.e., sec) we have to multiply our flipping times and MFPTs by $\beta L^2$, where $L$ is the length of the well and $\beta$ is the coefficient of viscous friction.

| | |
|---|---|
| For the flipping time | |
| (1) MFPT over high barrier | $E_0^{-2}e^{E_0+\Delta E}$ |
| (2) Inflection point | $2E_0^{-2}e^{E_0}$ |
| (3) MFPT over low barrier | $E_0^{-2}e^{E_0-\Delta E}$ |
| (4) MFPT over zero barrier | $\frac{1}{2}$ |
| For the MFPT | |
| (5) Low frequency limit | $E_0^{-2}e^{E_0+\Delta E}/2$ |
| (6) High frequency limit = MFPT (inflection point) | $E_0^{-2}e^{E_0}$ |
| (7) Minimum MFPT | $2E_0^{-2}e^{-E_0-\Delta E}$ |

Consider the kinetic scheme depicted below:




where $R+$ denotes the "reactant" state in the well with the barrier at $E_0+\Delta E$, and where $R-$ denotes the "reactant" state in the well with the barrier at $E_0-\Delta E$. Going into $P$, the absorbing product state, corresponds to escape after crossing the barrier. A kinetic description (which assumes instantaneous adiabatic adjustment) leads to a system of two coupled ordinary differential equations:

$$\begin{bmatrix}\dot r_+\\ \dot r_-\end{bmatrix}=\begin{bmatrix}-(\gamma+k_+) & \gamma\\ \gamma & -(\gamma+k_-)\end{bmatrix}\begin{bmatrix}r_+\\ r_-\end{bmatrix}. \qquad (14)$$

This system is easily solved; with $r_+(0)=r_-(0)=\frac{1}{2}$ the quantity $(r_++r_-)(t)$ describes the probability that a particle that was in $R+$ or $R-$ at time 0 (with a 50-50 probability distribution between $R+$ and $R-$) has not yet entered the absorbing state at time $t$. The MFPT is

$$\langle\tau\rangle^{\rm kin}=\int_0^\infty(r_++r_-)dt=\frac{k_++k_-+4\gamma}{2[k_+k_-+(k_++k_-)\gamma]}. \qquad (15)$$

Relating this back to Fig. 1 and substituting for $k_+$ and $k_-$ the approximate transition rates over nonfluctuating barriers at $E_0-\Delta E$ and $E_0+\Delta E$, respectively [neglecting

1 and $E_0$ relative to $\exp(E_0)$ in the sum and neglecting $\Delta E$ in the $(E_0 \pm \Delta E)^2$ factor], i.e.,

$$k_+ = E_0^2 e^{-E_0-\Delta E}, \quad k_- = E_0^2 e^{-E_0+\Delta E}, \tag{16}$$

gives us back formula (11) that we derived as a limit case of the FPE. We have thus matched the Brownian motion description with a kinetic description. From (15) we find

$$\frac{1}{\langle \tau \rangle^{\text{kin}}|_{\gamma=0}} = k^{\text{eff}}|_{\gamma=0} = \frac{2k_+k_-}{k_+ + k_-},$$
$$\frac{1}{\langle \tau \rangle^{\text{kin}}|_{\gamma\to\infty}} = k^{\text{eff}}|_{\gamma\to\infty} = \frac{k_+ + k_-}{2}. \tag{17}$$

We observe that the way the effective transition rate, $k^{\text{eff}}$, is composed of $k_+$ and $k_-$ at high and low frequency mimics two electrical resistors in parallel and series connection, respectively.

The agreement between the kinetic approximation and the actual MFPTs breaks down when the flipping time of the barrier is of the order of the MFPT over a constant zero barrier. We conjecture that this is the time scale at which adiabatic adjustment takes place.

In actual chemical reactions it takes about $10^{-12}$ to $10^{-9}$ sec to diffuse over a zero height barrier (i.e., the frequency factor in the transition state theory [9]). This means that for fluctuating or oscillating barriers in chemical transitions it is legitimate to use a kinetic approach so long as the frequency is less than about $10^9$ Hz.

This research was supported in part by NIH Grant No. RO1ES06010. We would like to thank V. Barcilon for useful discussions.

*Note added.*—Following submission of this paper, two additional articles on "resonant activation" have appeared from independent groups [10,11]. Both of these papers treat a kinetic approach to the problem of diffusion over a fluctuating potential, and Ref. [10] also gives a Fokker-Planck treatment to both a piecewise linear and piecewise constant potential. Equation (2) of Ref. [11] is essentially the same as Eq. (15) of the present paper. Neither of these papers shows a direct quantitative link between results obtained from solution of the Fokker-Planck equation with equations derived from a Markovian kinetic description.

[1] C. R. Doering and J. C. Gadoua, Phys. Rev. Lett. **69**, 2318 (1992).
[2] J. Maddox, Nature (London) **359**, 771 (1993).
[3] R. Zwanzig, Acc. Chem. Res. **23**, 148 (1990); J. Chem. Phys. **97**, 3587 (1992).
[4] C. W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 1985), 2nd ed.
[5] H. A. Kramers, Physica (Utrecht) **7**, 284 (1940).
[6] R. D. Astumian, P. B. Chock, T. Y. Tsong, and H. V. Westerhoff, Phys. Rev. A **39**, 6416 (1989).
[7] R. D. Astumian, P. B. Chock, T. Y Tsong, Y.-D. Chen, and H. V. Westerhoff, Proc. Natl. Acad. Sci. U.S.A. **84**, 434 (1987).
[8] Y.-D. Chen, Proc. Natl. Acad. Sci. U.S.A. **84**, 729 (1987).
[9] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941).
[10] U. Zurcher and C. R. Doering, Phys. Rev. E **47**, 3862 (1993).
[11] C. Van den Broek, Phys. Rev. E **47**, 4579 (1993).